Raman spectroscopy of stercorite $H(NH_4)Na(PO_4)\cdot 4H_2O$ – a cave mineral from Petrogale Cave, Madura, Eucla, Western Australia

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ABSTRACT

Raman spectroscopy complimented with infrared spectroscopy has been used to characterise the mineral stercorite $H(NH_4)Na(PO_4)\cdot 4H_2O$. The mineral stercorite originated from the Petrogale Cave, Madura, Eucla, Western Australia. This cave is one of many caves in the Nullarbor Plain in the South of Western Australia. These caves have been in existence for eons of time and have been dated at more than 550 million years old. The mineral is formed by the reaction of bat guano chemicals on calcite substrates. A single Raman band at 920 cm^{-1} defines the presence of phosphate in the mineral. Antisymmetric stretching bands are observed in the infrared spectrum at 1052, 1097, 1135 and 1173 cm^{-1}. Raman spectroscopy shows the mineral is based upon the phosphate anion and not the hydrogen phosphate anion. Raman and infrared bands are found and assigned to PO_4^{3-}, H_2O, OH and NH stretching vibrations. The detection of stercorite by Raman spectroscopy shows that the mineral can be readily determined; as such the application of a portable Raman spectrometer in a 'cave' situation enables the detection of minerals, some of which may remain to be identified.

KEYWORDS: stercorite, 'cave' mineral, brushite, mundrabillaite, archerite, Raman spectroscopy.

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INTRODUCTION

The mineral stercorite originated from the Petrogale Cave, Madura, Eucla, Western Australia. As such, many minerals formed in these caves include archerite $(K,NH_4)(H_2PO_4)$ [1], mundrabillaite $(NH_4)_2Ca(HPO_4)_2{\cdot}H_2O$ [2]. These minerals occur as stalactites and as crusts on the walls and floors of the caves. Other minerals found in the Petrogale cave include aphthitalite $(K,Na)_3Na(SO_4)_2$, halite NaCl, syngenite $(K,Na)_3Na(SO_4)_2$, stercorite $H(NH_4)Na(PO_4){\cdot}4H_2O$, oxammite $(NH_4)_2(C_2O_4) \cdot H_2O$, weddellite $Ca(C_2O_4){\cdot}2H_2O$, whitlockite $Ca_9Mg(PO_4)_6(HPO_4)$, guanine $C_5H_5N_5O$, newberyite $Mg(HPO_4){\cdot}3H_2O$ and calcite $CaCO_3$. These minerals are formed through the chemical reactions of calcite with bat guano or with chemicals from bat guano which are water soluble and crystallise out on the calcite surfaces. The mineral stercorite is water soluble and may translocate through the Petrogale cave network [3].

The name ‘stercorite’ is derived from the Latin word for ‘dung’. Stercorite is a triclinic mineral (pseudomonoclinic) [4] and is whitish to yellow in colour. This mineral belongs to space group 1bar with cell dimensions a = 10.636(2) b = 6.9187(14) c = 6.4359(13) α = 90.46(3) β = 97.87(3) γ = 109.20(3) with Z = 2 [4]. The mineral is congruent with respect to its components. Stercorite has a (100) layered structure built up by [010] rows of Na octahedra sandwiched between P tetrahedra; NH_4^+ and equivalent water molecules with tetrahedral environments, intercalate the layers and link them through H bonds [4]. The solubility and phase equilibrium diagram has been published [3].

The amount of published data on the Raman spectra of mineral phosphates is limited [5-9]. Further there is almost no data on the Raman spectroscopy of the phosphate 'cave' minerals. The Raman spectra of the hydrated hydroxy phosphate minerals have been reported only to a limited extent. In aqueous systems, Raman spectra of phosphate oxyanions show a symmetric stretching mode (ν_1) at 938 cm^{-1}, the antisymmetric stretching mode (ν_3) at 1017 cm^{-1}, the symmetric bending mode (ν_2) at 420 cm^{-1} and the ν_4 bending mode at 567 cm^{-1} [7, 8, 10]. More recent values have been reported by Rudolph and Irmer [11]. Density functional calculations enabled more precise measurements of the positions of the phosphate vibrational modes [11].

S.D. Ross in Farmer (1974) (page 404) listed some well-known minerals containing phosphate which were either hydrated or hydroxylated or both [12]. The value for the ν_1 symmetric stretching vibration of PO_4 units was given as 930 cm^{-1} (augelite), 940 cm^{-1} (wavellite), 970 cm^{-1} (rockbridgeite), 995 cm^{-1} (dufrenite) and 965 cm^{-1} (beraunite). The position of the symmetric stretching vibration is mineral dependent and a function of the cation and crystal structure. The fact that the symmetric stretching mode is observed in the infrared spectrum affirms a reduction in symmetry of the PO_4^{3-} units. This reduction in symmetry can be caused by site symmetry and/or factor group splitting.

Raman spectroscopy has proven most useful for the study of mineral structure [13-22]. The detailed comparative Raman spectra of the cave mineral stercorite have not been published. The objective of this research is to report the Raman and infrared spectra of stercorite and to relate the spectra to the mineral structure.

EXPERIMENTAL

Mineral

The mineral stercorite was supplied by The Australian Museum and originated from Petrogale Cave, Madura, Western Australia. Details of the mineral have been published (page 561) [23]. The mineral corresponds to the formula $H(NH_4)Na(PO_4)\cdot 4H_2O$.

Raman spectroscopy

Crystals of stercorite were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10x, 20x, and 50x objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a CCD detector (1024 pixels). The Raman spectra were excited by a Spectra-Physics model 127 He-Ne laser producing highly polarised light at 633 nm and collected at a nominal resolution of 2 cm^{-1} and a precision of ± 1 cm^{-1} in the range between 100 and 4000 cm^{-1}. Repeated acquisition on the crystals using the highest magnification (50x) was accumulated to improve the signal to noise ratio in the spectra. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer.

Infrared spectroscopy

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the 4000–525 cm^{-1} range were obtained by the co-addition of 128 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 cm/s. Spectra were co-added to improve the signal to noise ratio.

Band component analysis was undertaken using the Jandel 'Peakfit' (Erkrath, Germany) software package which enabled the type of fitting function to be selected and allowed specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentz-Gauss cross-product function with the minimum number of component bands used for the fitting process. The Lorentz-Gauss ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations (r^2) greater than 0.995. Band fitting of the spectra is quite reliable providing there is some band separation or changes in the spectral profile.

RESULTS AND DISCUSSION

The Raman spectrum of stercorite over the 800 to 1100 cm^{-1} and the infrared spectrum over the 800 to 1200 cm^{-1} range are displayed in Figs. 1a and 1b respectively. The complete Raman and infrared spectrum over the full wavenumber range is given in Fig. S1 in the supplementary information. A single band at 920 cm^{-1} is observed in the Raman spectrum (Fig. 1a) and is assigned to the ν_1 PO_4^{3-} symmetric stretching mode. The observation of a single band is perhaps unexpected, as with three different cations in the mineral structure, it

might be expected that the band would split into component bands. Further the single band observed in the Raman spectrum suggests that the symmetry of the phosphate anion is preserved in the mineral structure. In addition, the presence of the proton might suggest the existence of HPO_4^{2-} ions. If this is the case then again two symmetric phosphate stretching modes would be observed. This is not the case.

In the infrared spectrum (Fig. 1b) two low intensity bands at 989 and 1010 cm^{-1} are attributed to this vibrational mode. An intense infrared band is found at 1097 cm^{-1} with component bands at 1052, 1135 and 1173 cm^{-1}. These bands are attributed to the ν_3 PO_4^{3-} antisymmetric stretching mode. Raman bands in these positions were not observed. In the infrared spectrum, some low intensity bands are observed at 817, 871, 900 and 934 cm^{-1}. The assignment of these bands have two possibilities: highly likely are water librational modes and secondly the band at 871 cm^{-1} may be due to the symmetric stretching mode of HPO_4^{2-} units. However no bands in this position were observed in the Raman spectrum. This mitigates against this assignment.

The Raman spectrum over the 300 to 650 cm^{-1} range and the infrared spectrum over the 550 to 800 cm^{-1} range are displayed in Figs. 2a and 2b. Two Raman bands are resolved at 450 and 476 cm^{-1} and are attributed to the PO_4^{3-} ν_2 bending mode. The observation of two bands suggests some distortion of the phosphate anion, perhaps brought about by the position of the different cations around the phosphate anion. The bands are not observed in the infrared spectrum as the position of the bands lies below the detection limit of the instrumentation. The two ν_2 infrared bands for pseudomalachite published by Farmer [12] were reported at 450 and 422 cm^{-1}. For pseudomalachite Raman bands were observed at 482 and 452 cm^{-1} with equal intensity. Cornetite Raman spectrum showed an intense band at 433 cm^{-1} with minor components at 463 and 411 cm^{-1}. Farmer [12] reported two bands at 464 and 411 cm^{-1} for cornetite. Farmer [12] also reported a number of bands of phosphate minerals in the 480 to 680 cm^{-1} region and ascribed these bands to the ν_4 modes. The intense infrared band at 615 cm^{-1} with a shoulder on the low wavenumber side at 601 cm^{-1} is attributed to the ν_4 vibrational modes. The Raman band at 577 cm^{-1} may be the equivalent of this vibration observed in the infrared spectrum. The assignment of these bands is consistent with the data

reported by Farmer [12] in a series of Tables including Table 17. XV in which a wide range of hydrated divalent phosphates including the ammonium ion. In the infrared spectrum bands are observed at 755 and 773 cm^{-1}. These bands are assigned to water librational modes. Raman bands observed at 326, 345 and 396 cm^{-1} are considered to be related to the hydrogen bonding of the water to the phosphate units in the stercorite structure. The first two bands might be assigned to the ν_2 bending modes of the PO_4^{3-} ion.

The Raman spectrum over the 50 to 300 cm^{-1} range and the infrared spectrum over the 1200 to 1800 cm^{-1} range are displayed in Figs. 3a and 3b. Raman bands are observed at 110, 143, 155, 185, 197 and 216 cm^{-1} and are simply described as lattice vibrations. The infrared peak centred upon 1631 cm^{-1} is complex and a series of overlapping bands may be resolved. These bands are attributed to water HOH and ammonium HNH bending modes. The infrared bands at 1260, 1318, 1405 and 1443 cm^{-1} are attributed to NH_4^+ vibrations. Farmer tabulated NH_4^+ vibrations in the 1410 to 1475 cm^{-1} range for ammoniated divalent phosphates (Table 17. XV) and defined these bands as NH_4^+ ν_4 bending modes.

The Raman spectrum of stercorite over the 2700 to 3500 cm^{-1} range and the infrared spectrum over the 2900 to 3700 cm^{-1} range are displayed in Figs. 4a and 4b. Raman bands are observed at 2900, 3024 and 3158 cm^{-1}. The first band is assigned to the NH stretching vibration of the NH_4^+ units. The position of these bands suggests that the water is involved in strong hydrogen bonding. The latter two bands are due to water stretching vibrations. In the infrared spectrum four bands are observed at 3066, 3232, 3340 and 3578 cm^{-1}. These bands are at higher wavenumbers than those in the Raman spectrum.

Mechanism of formation of stercorite

In the laboratory, the mineral is readily synthesised by mixing aqueous solutions of sodium hydrogen phosphate Na_2HPO_4 and ammonium hydrogen phosphate $(NH_4)_2HPO_4$ [3]. Platford [3] showed that the two chemicals were in congruency with their components. It is likely that low temperatures aid the formation of stercorite, as might occur in caves on the

Nullarbor Plains in Western Australia. Whether or not the mineral stercorite is formed by simply solubility effects from undersaturated solutions is open to question, but it does seem likely. The presence of the calcite surface serves as a surface for the crystallisation of the stercorite.

CONCLUSIONS

The mineral stercorite is an ammoniated hydrogen sodium phosphate and is found in caves in Western Australia and is especially known from the Petrogale Cave, near Madura, Western Australia. The mineral has also been found Ichaboe Island, Namibia and Gua˜nape Island, Peru. It is a mineral formed by the reaction of calcite with bat (or bird) guano. The mineral is associated with other phosphate minerals including struvite, archerite, brushite. According to Platford [3], the mineral is formed from solution. Hence the basic components of the mineral can be translocated through a cave system.

The mineral because of the individual vibrating units, lends itself to vibrational spectroscopy. A combination of Raman and infrared spectroscopy has been used to identify vibrational modes associated with the mineral stercorite. The question arises as to whether the mineral contains hydrogen phosphate units or simply phosphate units. Based upon Raman spectroscopy the anion in the mineral is the phosphate anion and no observation of hydrogen phosphate units were found. The detection of stercorite by Raman spectroscopy shows that the mineral can be readily determined; as such the application of a portable Raman spectrometer in a ‘cave’ situation enables the detection of minerals in cave systems, some of which remain to be identified.

Acknowledgments

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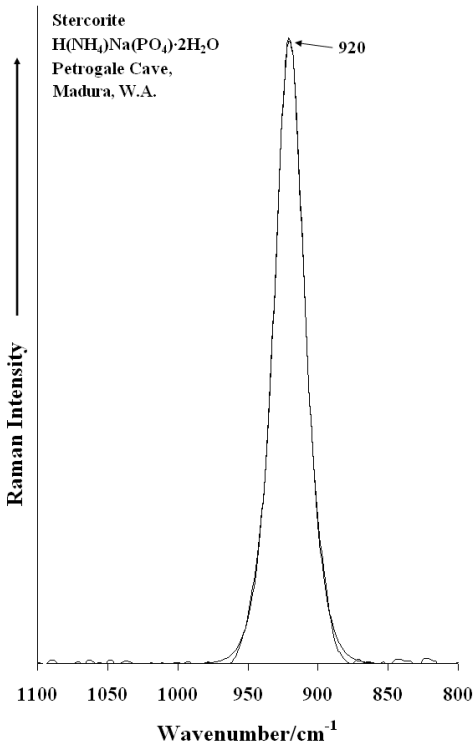

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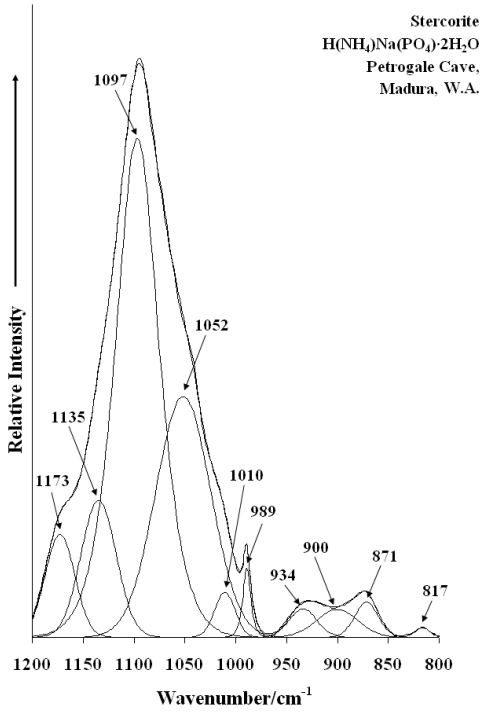

Fig.1b

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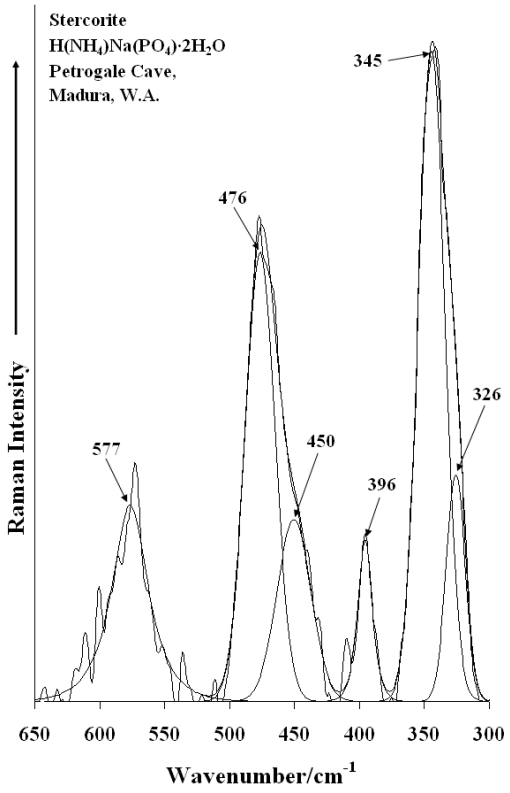

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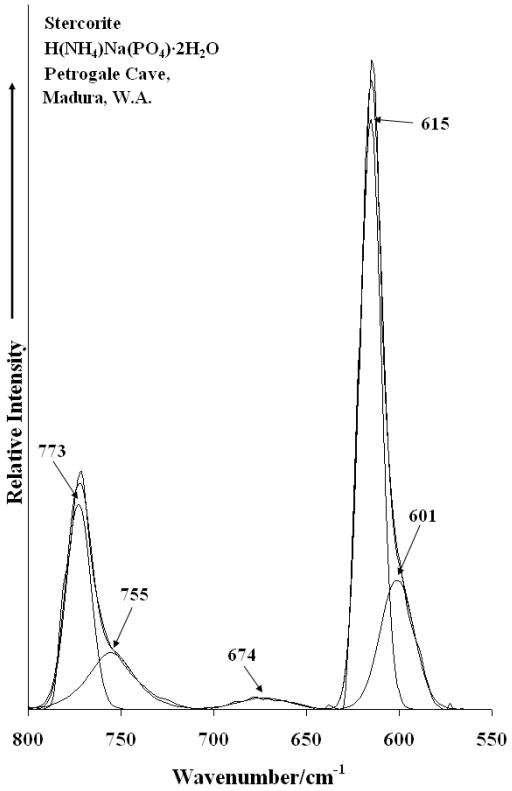

Fig. 2b

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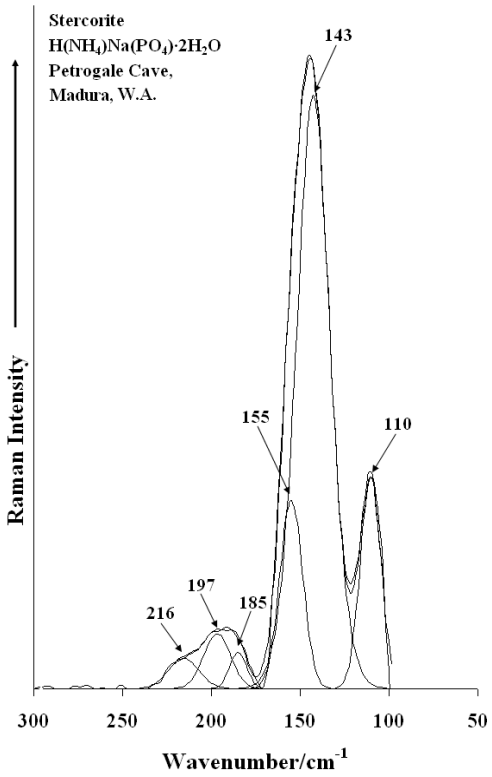

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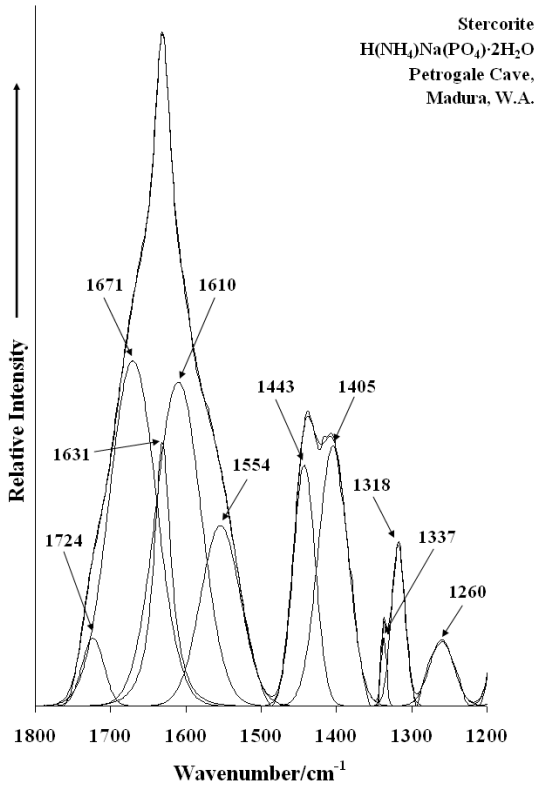

Fig. 3b

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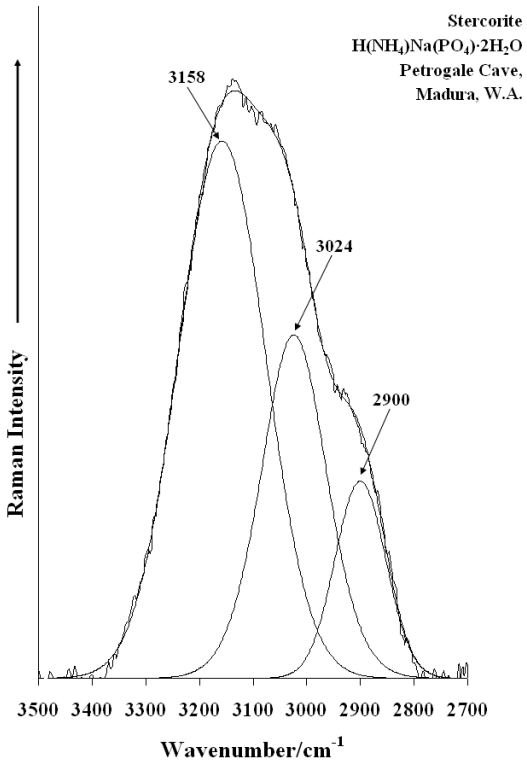

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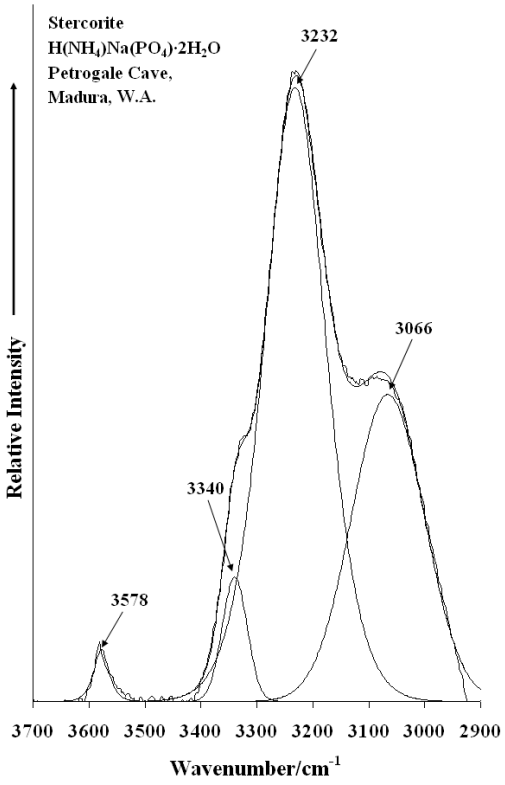

Fig. 4b

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